Supporting Information

Continuous Coordination Modulation with Differing Heteroatoms Unveils Favorable Single-atom Ni Sites for Near-unity CO Selectivity in CO₂ Electroreduction

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Experimental section

Chemicals

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, 98%) was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China). Nickel chloride hexahydrate (NiCl₂·6H₂O, 99%) and sulfuric acid (H₂SO₄, 98%) were obtained from Kelong Chemical Co., Ltd. (Chengdu, China). Ammonium chloride (NH₄Cl, 99%) and potassium carbonate (K₂CO₃, 99.999%) were sourced from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). All chemicals were used without further purification. Aqueous solutions were prepared with Millipore water (18.2 M Ω ·cm⁻¹). Carbon paper (TGP-H-060, Toray) was acquired from Fuel Cell Store.

Synthesis of Ni single-atom catalysts (Ni SACs)

The Ni SACs were synthesized using the following procedure. In a typical synthesis, PTCDA (100 mg, 0.25 mmol), NiCl₂·6H₂O (237 mg, 1 mmol), and NH₄Cl (5 g, 93.47 mmol) were weighed into a mortar and thoroughly ground to obtain a uniform mixture. The resulting mixture was then transferred to a tube furnace and annealed at 1000 °C for 2 hours under argon gas, with a ramping rate of 3 °C/min. Subsequently, the fluffy black sample was dispersed in 1 M H₂SO₄ solution at 80 °C for 12 hours to remove unstable metallic species. The final product (N₃Ni–C) was washed several times with ultrapure water and dried in vacuum at 80 °C for 12 hours. N₃Ni–O and N₃Ni–N were synthesized using the same procedure, with the annealing temperatures adjusted to 800 °C and 900 °C, respectively. The comparative sample CN was prepared similarly, but without the addition of NiCl₂·6H₂O. Notably, NH₄Cl was selected as the nitrogen source because, during pyrolysis, it releases HCl, which can effectively suppress metal species agglomeration by forming volatile metal chlorides and etching loosely bound clusters, thus promoting the formation of atomically dispersed metal sites.¹

Material characterization

Transmission electron microscopy (TEM) images, energy dispersive X-ray (EDX)

elemental mapping, and high-angle annular dark-field scanning TEM (HAADF-STEM) images were acquired using a Talos 200 S/TEM (Thermo Fisher Scientific) operating at 200 kV. Atomic-resolution HAADF-STEM images were obtained with a double Cscorrected transmission electron microscope (Thermo Fisher Spectra 300) operating at 300 kV from FEI company. X-ray photoelectron spectroscopy (XPS) analyses were performed using an ESCALAB 250Xi system equipped with a monochromatic Al Ka Xray source under ultrahigh vacuum conditions. All spectra were calibrated using the C 1s peak at 284.8 eV as a reference binding energy. X-ray diffraction (XRD) measurements were conducted on a PANalytical X'Pert Powder Advance diffractometer using Cu Ka radiation. X-ray absorption spectra (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the Ni K-edge, were collected at the 1W1B station of the Beijing Synchrotron Radiation Facility (BSRF), P.R. China. The BSRF storage rings were operated at 2.5 GeV with a maximum current of 250 mA. Data were collected at room temperature in fluorescence mode using N₂-filled ionization chambers. Energy calibration was performed using Ni foil. The spectra were analyzed using the Athena software package. N₂ adsorption-desorption isotherms were measured on a BELSORP MAX instrument from MicrotracBEL to estimate the surface area of the samples using the Brunauer-Emmett-Teller (BET) method at 77 K. Raman spectra were collected using a HORIBA HR Evolution spectrometer with a 532 nm laser, covering the range from 200 to 3000 cm⁻¹. The elemental composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Spectro GREEN instrument. Liquid products were analyzed by ¹H nuclear magnetic resonance (¹H NMR) spectroscopy using a Bruker 400 MHz spectrometer, with dimethyl sulfoxide (DMSO) as an internal standard.

Electrochemical measurement

Electrolysis in H-type Cell: Electrochemical measurements were conducted in a gastight H-type electrochemical cell using a BioLogic VMP3 workstation at room temperature. The reaction cell was divided into cathode and anode chambers by a 117 membrane (DuPont). A platinum sheet (1 cm × 1 cm) and Ag/AgCl (saturated KCl)

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electrodes served as the counter and reference electrodes, respectively. Unless otherwise specified, all potentials in this study were measured against the Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale using the formula:

E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.0591 × pH + 0.197

The working electrode was prepared by depositing 0.5 mg of catalyst on hydrophobic carbon paper (CP, 1×1 cm²). Catalyst ink was prepared by dispersing 5 mg of catalyst in 950 µL ethanol and 50 µL Nafion solution (5 wt%, DuPont), followed by ultrasonic treatment for 30 minutes. Subsequently, 50 µL of the ink was evenly deposited onto the hydrophobic CP and dried at room temperature. Each cell chamber was filled with 20 mL of CO₂-saturated 0.5 M KHCO₃ (pH = 7) as the electrolyte during the electrocatalytic process. The electrolyte was purged with N₂ or CO₂ for at least 20 minutes prior to electrolysis. During measurements, the CO₂ flow rate was maintained at 20 mL min⁻¹ using a mass flow meter, and gas was continuously bubbled into both chambers. The cathodic electrolyte was stirred at 600 rpm. All electrochemical measurements were conducted with 85% iR compensation, and linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV/s from –1.3 to 0 V_{RHE}.

Electrolysis in Flow Cell: Flow cell measurements were carried out in a homemade flow reaction cell, which primarily consists of a CO₂ flow chamber, cathode, and anode liquid flow compartments. The catalyst, loaded at 0.5 mg cm⁻² onto a gas diffusion electrode (GDE, reaction area of 1 cm²), was used as the working electrode. An Hg/HgO electrode served as the reference electrode, while iridium oxide loaded on carbon paper (IrO₂/carbon paper) was used as the counter electrode. The potential was converted to the reversible hydrogen electrode (RHE) scale using the formula:

E (V vs. RHE) = E (V vs. Hg/HgO) + 0.0591 × pH + 0.098

During electrochemical measurements, the anolyte and catholyte (1 M KOH, pH = 13.8) were separated by an anion exchange membrane and individually circulated using a peristaltic pump. The CO₂ flow rate was maintained at 30 mL min⁻¹, controlled by a mass flow meter. All electrochemical measurements were conducted with iR compensation.

For determining the electrochemical surface area (ECSA), we employed the doublelayer capacitance method in a 0.5 M KHCO₃ solution at non-Faradaic potentials ranging from -0.05 to 0.05 V_{RHE}. The measurements were conducted with scan rates varying from 5 to 30 mV/s.

For product analysis, we utilized online gas chromatography (GC-9860-5C-NJ) equipped with a thermal conductivity detector (TCD) and two flame ionization detectors (FID) for continuous analysis. High-purity argon (99.999%) served as the carrier gas for gas chromatography, and the quantification of each gas was performed using the external standard method. Liquid products were primarily analyzed by collecting ¹H NMR spectra using a 400 MHz NMR spectrometer (AVANCE NEO 400) with water suppression capabilities. The NMR sample solution consisted of 500 μ L of electrolyte, collected after 70 minutes of CO₂ reduction electrolysis, and 100 μ L of dimethyl sulfoxide (DMSO) as an internal standard (50 ppm in D₂O). Unless otherwise specified, all chronoamperometry data were obtained by conducting measurements at each potential for 70 minutes, with the process repeated three times.

The Faradaic efficiency (FE) of CO or H₂ was calculated using the fellow equation:

$$FE = \frac{2FvcP_0}{jTR}$$

Where, F is the Faraday constant (96485 C mol⁻¹); v is the gas flow rate; c is the measured concentration of the product by GC; P_0 is 101 kPa; j is the total current; T is 273.15 K; R is the gas constant (8.314 J mol⁻¹ K⁻¹).

The partial current density of CO (j_{co}) was converted from the following formula:

$$j_{CO} = FE_{CO} \times j$$

j is the total current.

The turnover frequency (TOF) value of the electrocatalyst was calculated using the formula below:

$$TOF = \frac{j_{CO}/2F}{m_{cat} \times w/M_{Ni}} \times 3600$$

Where, j_{CO} is partial current density of CO; F is the Faraday constant (96485 C mol⁻¹); m_{cat} is the mass of the catalyst loaded on the working electrode.; w is the mass fraction of Ni in catalyst; M_{Ni} is the atomic mass of Ni (58.69 g mol⁻¹).

Operando ATR-SEIRAS spectroscopy

Operando attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was conducted using a modified H-type electrochemical cell, with 20 mL of 0.5 M KHCO₃ solution in each compartment, separated by a 117 membrane (DuPont). Spectral signals were collected using a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, USA). Before the experiment, the system was purged with CO₂ for 30 minutes to remove air and achieve CO₂ saturation in the KHCO₃ solution. The working electrode, reference electrode, and counter electrode were a gold-coated single-crystal silicon substrate with catalyst deposition, a saturated Ag/AgCl electrode, and a Pt wire, respectively. Background spectra were collected without applying voltage, and subsequent spectra were acquired with a resolution of 8 cm⁻¹, and each spectrum was scanned 32 times.

Computational Models and Methods

For modelling Ni single atom catalyst with different coordination, a 4×4 supercell slab of the graphene single layer was built with a 15 Å vacuum gap to avoid interlayer interactions. To anchor the metal single atom, the 2 adjacent carbon atoms were removed and the 4 nearest-neighbored carbon atoms are replaced with N atoms or O atoms, as shown in Fig. S16. The formation of three important reaction intermediates including COOH^{*}, CO^{*} and H^{*} (* is the clean surface) over N₃Ni–O, N₃Ni–N, and N₃Ni–C were investigated. The optimized configurations of these reaction intermediates are shown in Fig. S17.

The eCO₂RR into CO and the HER over Ni single atom catalysts were investigated by using density-functional theory (DFT) calculations, which were performed by using the Vienna ab initio simulation package (VASP) with the Perdew-Burke-Ernzerhof functional.²⁻⁴ We expanded wave functions in plane waves with an energy cutoff of 400 eV. A Monkhorst-Pack 3×3×1 mesh was used in the first Brillouin zone for simulating reactions. Spin-polarized DFT calculations were performed by enabling the SPIN and MAGMOM settings. The convergence criteria for electronic relaxation is 10⁻⁵

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eV, and 0.01 eV/Å for ionic relaxation.

The Gibbs free energy (ΔG) of the main reaction intermediates are calculated by using the equation of

$\Delta G = \Delta EDFT + \Delta ZPE + \Delta GU + \int CpdT - T\Delta S$

where Δ EDFT is the calculated DFT energy of the reaction system, ZPE is zero-point energy, $\int CpdT$ is the enthalpic correction and Δ S is entropy contribution to the total Gibbs free energy. $\Delta G_U = -neU$, where n is the number of electrons transferred and U is the electrode potential versus the reversible hydrogen electrode (RHE). We took a clean surface as a reference and drew free energy diagrams at T= 298.15 K, the potential of $-0.70 V_{RHE}$. Supplementary Figures and Tables



Fig. S1 Morphology characterization and chemical structure of PTCDA. (a) Lowmagnification TEM image. (b) High-magnification TEM image.



Fig. S2 Morphology and composition characterization of CN. (a) TEM image. (b-d) HAADF-STEM and elemental mapping images.



Fig. S3 Raman spectra of N_3Ni-C , N_3Ni-N , and N_3Ni-O .



Fig. S4 (a) N_2 isothermal adsorption-desorption curve and (b) pore size distribution of N_3Ni-C , N_3Ni-N , and N_3Ni-O .

Note: The pore size distribution indicates that N₃Ni–C and N₃Ni–N possess more abundant microporous structures, with dominant pore sizes around 0.5 nm, compared to N₃Ni–O (**Fig. S4b**). This enhanced microporosity accounts for the increased surface areas of the former two samples (inset of **Fig. S4a**). The formation of these micropores is likely induced by temperature-driven structural defects or wrinkling during hightemperature treatment. Since N₃Ni–C and N₃Ni–N were synthesized at higher pyrolysis temperatures than N₃Ni–O, they consequently exhibit more pronounced microporosity.



Fig. S5 Morphology and composition characterization of N_3Ni –O. (a) TEM image. (b) AC HAADF-STEM image. (c), (d) HAADF-STEM and elemental mapping images.



Fig. S6 Morphology and composition characterization of N₃Ni–N. (a) TEM image. (b) AC HAADF-STEM image. (c) HAADF-STEM and elemental mapping images.



Fig. S7 The fitting curves of Ni foil, NiO and NiPc.



Fig. S8 LSV of N_3Ni-C in 0.5 M KHCO₃ saturated with CO_2 (red line) and Ar (blue line).



Fig. S9 ^1H NMR spectroscopy in D2O of 0.5 M KHCO3 electrolyte after the eCO2RR at $-0.7~V_{\text{RHE}}.$



Fig. S10 The total current density of N_3Ni-C , N_3Ni-N , N_3Ni-O , and CN.



Fig. S11 The Tafel plots of N_3Ni-O , N_3Ni-N , N_3Ni-C , and CN in CO_2 -saturated 0.5 M KHCO₃ electrolyte.



Fig. S12 Cyclic voltammograms (CV) curves under different scan rates for (a) N₃Ni–O, (b) N₃Ni–N, and (c) N₃Ni–C. (d) Charging current density differences j plotted against scan rates for the different catalysts.



Fig. S13 XRD pattern of the N₃Ni−C catalyst before and after the long-term stability test.



Fig. S14 The morphology and elemental mappings of N₃Ni–C after the long-term stability test. (a) Low-magnification TEM image. (b) High-magnification TEM image. (c) HAADF-STEM and elemental mapping images.



Fig. S15 The AC HAADF-STEM image of N_3Ni-C after the long-term stability test.



Fig. S16 (a) Molecular structure of the carbon precursor, PTCDA ($C_{24}H_8O_6$) and (b) Optimized structure of NiN₃–O and NiN₃–O _{vertical} (O unbonded to C) and their energy difference.

Note: The O atom in Ni–O is bonded to the C matrix, as supported by the following key points: (1) The oxygen in Ni–O originates from the incomplete volatilization of oxygen in the carbon precursor, PTCDA, which has a planar structure where oxygen atoms are directly bonded to carbon (**Fig. S16a**), promoting the formation of a N₃Ni–O planar geometry and enabling O–C linkage. (2) DFT calculations show that the system energy is 4.86 eV higher when the O atom in Ni–O is not bonded to carbon, indicating that the unbonded configuration is thermodynamically unfavorable (**Fig. S16b**). (3) Charge density difference analysis reveals electron redistribution among Ni, O, and C atoms (**Fig. 2f–h**), further supporting the bonding interactions between them.



Fig. S17 Simulation models of N₃Ni–O, N₃Ni–N, and N₃Ni–C.



Fig. S18 Optimized structures of the formation of COOH*, CO*, and H* on N₃Ni–O, N₃Ni–N, and N₃Ni–C.



Fig. S19 The adsorption energy of COOH intermediate (E_{COOH}) on the three catalysts. The difference of limiting potentials (U_L) between eCO₂RR and HER.



Fig. S20 The charge density difference for COOH adsorption on (a) N_3Ni-O , (b) N_3Ni-N , and (c) N_3Ni-C .

Sample	Shell	CN	<i>R</i> (Å)	σ^2 (Å 2)	<i>ΔE₀</i> (eV)	R factor
Ni Foil	Ni–Ni	12	2.48	0.006	7.27	0.002
NiO	Ni–O	5.4	2.07	0.005	-1.64	0.006
NiPc	Ni–N	4.43	1.90	0.004	1.65	0.023
N₃Ni–O	Ni–N	2.93	1.91	0.008	-4.12	0.007
	Ni–O	0.96	2.10	0.003		
N ₃ Ni–N	Ni–N	3.74	1.88	0.002	-12.95	0.007
N₃Ni–C	Ni–N	3.15	1.88	0.008	-8.02	0.006
	Ni–C	1.33	2.11	0.002		

Table S1. Fitting parameters of Ni K-edge EXAFS were obtained for various Ni SACs.

 S_0^2 , the amplitude reduction factor, was set to 0.811 based on fitting the known coordination number of 12 for Ni foil. *CN*: coordination numbers; *R*: bond distance; σ^2 : Debye-Waller factors; ΔE_0 : the inner potential correction. *R* factor: goodness of fit.

-jco Electrolyte TOF Atomic Potential FE_{co} Catalyst (mA Ref. (KHCO₃) (s⁻¹) configuration (V_{RHE}) (%) cm⁻²) This 0.5 M 99.3 N₃Ni–C N₃−Ni−C -0.7 12.1 5.89 work 15 0.5 M 92 ~4.00 Ni₁-NSC Ni–N₃–S -0.78 10.5 Ni SAs/ ~99 26 O-Ni-N₄ 0.5 M -0.77 21 3.05 OMMNC Ni-N-C 0.5 M -0.7 98.5 37 $Ni-N_2$ 38 -4⁸ Ni-NCN Ni–N4 0.5 M 96.6 -0.83 10 2.96 5⁹ Ni-SA-BB/C $Ni-N_4$ 0.5M -0.9 96.8 7.2 ~0.5 O-Ni-N₄ 6¹⁰ Ni-NUK-900 0.5M -0.73 94 3.6 3.16 711 Ni-NC(HPU) Ni–N₄ 0.5M -0.8 91 27 -8¹² Ni-SAC@NC Ni–N₃ 0.5M -0.6 95 5.7 1.44 ~99 ~9 9¹³ Ni@C₃N₄-CN $Ni-N_4$ 0.5 M -0.87 6.11 10¹ Ni-NC(AHP) 0.5 M ~100 14.5 Ni–N4 -0.9 -11¹⁴ Ni-N₄-O/C O-Ni-N4 99.2 0.5 M -0.9 23 3.11 **CNS-NiSA** 12¹⁵ Ni−N₃−S 0.5 M -0.8 95 7.8 0.51 Ni-N₃-C 95.6 13¹⁶ $Ni-N_3$ 0.5 M -0.65 6.6 0.40 Ni SAs -0.5 M -0.8 97 6.8 1.80 14¹⁷ Ni-N-MEGO Ni–N₄ 0.5 M -0.65 92 20 0.24 15¹⁸ 16¹⁹ A-Ni-NG Ni–N4 0.5 M -0.72 97 22 4.11 SE-Ni 17²⁰ $Ni-N_3$ 0.5 M -0.8 96 ~8 13.56 SAs@PNC 18²¹ Ni-NG Ni–N–C₃ 0.5 M -0.74 ~95 11 -NiSAs/N-C 0.5 M 19²² Ni–N₃ -1 72 7.5 1.46 Ni-N-C -0.78 20²³ Ni–N4 0.1 M 85 10.2 -

Table S2. Comparison of the eCO_2RR performance of N_3Ni-C with that reported in the published literature in H-cell.

Table S3. Comparison of the eCO_2RR performance of N_3Ni-C with that reported in the published literature in flow cell.

Catalyst	Atomic configuration	Electrolyte	FE _{CO} (%)	-j _{co} (mA cm ⁻²)	Ref.
N₃Ni–C	N₃–Ni–C	1 М КОН	99.2	396.8	This work
Ni-SA-BB/C	Ni–N4	1 M KOH	99.8	85.2	1 ⁹
Ni-NUK-900	O–Ni–N4	1 M KOH	83.7	100	2 ¹⁰
Ni-NCN	Ni–N4	0.5 M KHCO₃	97.9	100.2	3 ⁸
Ni-SAs@BNC	Ni–N4	0.5 M KHCO ₃	97	207.6	4 ²⁴
C800NiA	Ni–N _{4-x} –C _x	1 M KOH	~99	297	5 ²⁵
Ni-N ₄ /C-NH ₂	Ni–N4	1.0 М КОН	89	327.8	6 ²⁶
Ni@NiNCM	Ni–N4	1.0 M KHCO₃	93.7	100	7 ²⁷
Ni-NCB	Ni–N4	0.1 M KHCO₃	99	>100	8 ²⁸
Ni-N-C	Ni–N4	1 M KHCO₃	85	199.8	9 ²⁹
3D-Ni-SAC	Ni–N4	0.5 M KHCO₃	93	325.5	10 ³⁰
Ni ₁ -NSC	Ni–N₃–S	0.5 M KHCO₃	~100	350	11 ⁵
Ni-N ₁ -C ₃	Ni–N–C ₃	1 M KOH	99	207	12 ³¹
A-Ni@CMK	Ni-N4	1.0 М КОН	99.5	247	13 ³²
NiSA/PCFM	Ni-N4	0.5 M KHCO₃	88	308.4	14 ³³

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